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SYNTHESIS OF NEW SUPERHARD MATERIALS AND THEIR APPLICATION TO CUTTING TOOLS

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OXIDES	PERFORMANCE	TOOL LIFE

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The process of Activated Reactive Evaporation is used to synthesize superhard materials like carbides, oxides, nitrides and ultrafine grain cermets. The deposits are characterized by hardness, microstructure, microprobe analysis for chemistry and lattice parameter measurements. The synthesis and characterization of TiC-Ni cermets and Al_2O_3 are given. High speed steel tool coated with TiC, TiC-Ni and TaC are tested for machining performance at different speeds and feeds. The machining evaluation and the selection of coatings is based on the rate of deterioration of the coating tool temperature, and cutting forces. Tool life →

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cont.

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SYNTHESIS OF NEW SUPERHARD MATERIALS AND THEIR APPLICATION TO CUTTING TOOLS

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SYNTHESIS OF NEW SUPERHARD MATERIALS AND THEIR APPLICATION TO CUTTING TOOLS

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ABSTRACT

Two major areas of effort are encompassed:

I. <u>Synthesis of Superhard Materials</u>: The process of Activated Reactive Evaporation is used to synthesize superhard materials like carbides, oxides, nitrides and ultrafine grain cermets. The deposits are characterized by hardness, microstructure, microprobe analysis for chemistry and lattice parameter measurements. The synthesis and characterization of TiC-Ni cermets and Al_2O_3 is given.

II. <u>Study and the Effect of Superhard Coatings on the Performance of High Speed Steel Tools</u>: High speed steel tools coated with TiC, TiC-Ni and TaC are tested for machining performance at different speeds and feeds. The machining evaluation and the selection of coatings is based on the rate of deterioration of the coating, tool temperature, and cutting forces. Tool life tests show coated high speed steel tools having 150 to 300% improvement in tool life compared to uncoated tools. Variability in the quality of the ground edge on high speed steel inserts produce a great scatter in the machining evaluation data.

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I. OBJECTIVE

The objectives of this research are two-fold: Firstly, the synthesis
of new superhard materials. Secondly, to examine the effect of superhard
coatings on the performance of high speed steel cutting tools. Such applica-
tions as well as others, e.g., grinding tools, hard coatings for abrasion and
wear resistance in engines, aircraft, tanks, metal forming machinery, dies,
punches, etc., could be of great interest to the DOD.

There are several reasons for concentrating the application effort on
cutting tools in general and high speed steel tools in particular. Firstly,
very little work has been carried out in the application of hard carbide
coatings to improve the life of high speed steel tools (single point tools,
end mills, cutters, etc.) even though they form the largest single item in
the tool production of cutting tools; the present mill shipments of high speed
steel tools is estimated at $800 million. Secondly, the Activated Reactive
Evaporation (ARE) process, recently developed at UCLA under ARPA sponsorship,[1]
is uniquely suited for this purpose since the hard coating can be applied
even at low substrate temperatures, i.e., about 500°C, which would still
retain the substrate (high speed steel tools) in its hardened and tempered
condition without softening. Competing processes such as chemical vapor
deposition require that the substrate be at temperatures of 1000°C or higher
for the deposition of hard compounds such as TiC which would, of course, ruin
the strength and toughness of the high speed steel. Such CVD processes are
commercially used today to coat TiC onto a WC-Co type carbide machining
inserts which can withstand high deposition temperatures (1000°C). Hard
coating can also be laid down by sputtering; however, the deposition rates
from sputtering are very low.

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In the Activated Reactive Evaporation process, Bunshah and his
co-workers[1,2] have developed a new high rate physical vapor deposition process
for the synthesis of oxides, nitrides and carbides. Furthermore, they found
that by controlling the deposition temperature or by heat-treatment,[3] it was
possible to change the microstructure and consequently increase the hardness
of TiC from 3000 to 5400 kg/mm, a value second only to diamond (see Table I)
and comparable to or better than the second hardest material known, borazon
(cubic boron nitride). Moreover, TiC should cost 100 times less than borazon
or diamond, which is a considerable economic incentive. Finally, high speed
steel (a strong and tough material) coated with a superhard layer such as TiC
or other materials, would be an ideal system to study for improved tool per-
formance since the necessary requirements of hardness for cutting and tough-
ness to absorb the impact loads are fulfilled by this composite system.

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TABLE I
Hardness of Various Materials

Material	Knoop Hardness (kg/mm^2)		Wooddell Scale (relative)
	Room Temperature	900°C	Room Temperature
Diamond	7000		43
Borazon (cubic/boron nitride)	4700		19
Samarium Borides (Sm B$_{\sim 2}$)	3610		
(Sm B$_{\sim 70}$)			
Rare Earth Borides (REB$_{70}$)	3500–4000		
Titanium Carbide*	3000	400	
Hafnium Carbide	2400	800	
Vanadium Carbide	2400	400	
Silicon Carbide	2480		14
Niobium Carbide	2200	500	
Aluminum Oxide	2100		9
Tungsten Carbide	1850	1200	
Tantalum Carbide	1700	400	
Chromium Carbide (Cr_7C_3)	1500	600	
Chromium Carbide ($Cr_{23}C_6$)	950	700	
Quartz	820		7

_____

*The hardness of TiC produced by Activated Reactive Evaporation can be as high as 5400 kg/mm^2.

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II.   RESEARCH PROGRAM

The proposed research program is divided into the following two parts:

A.   Synthesis of New Superhard Materials

The Activated Reactive Evaporation (ARE) process will be used to synthesize new superhard materials such as carbides, nitrides, oxides and two-phase alloys. The ARE is a versatile process that is capable of the following:

1) Synthesizing oxides, carbides, nitrides and possibly borides and silicides.

2) Synthesizing mixed carbides (i.e., carbides of more than one metal) of controlled composition, e.g., (TiZr)C.

3) Synthesizing mixed compounds (i.e., carbo-nitrides, oxy-carbides, etc.)

4) Changing the microstructure and mechanical properties by variation of process parameters, e.g., (deposition temperature).

5) Producing material ranging from full density coatings all the way to powder.

6) Producing very fine grain sizes.

7) Varying and controlling the stoichiometry of carbides and other compounds.

8) Laying down a deposit which is strongly adherent to the substrate due to a diffusion bond produced between the two.

9) Producing graded microstructures, e.g., from metal to carbide.

10) Obtaining high deposition rates for coatings (5 to 25 μ per minute) which make it an economical process.

This part of the research program will be concentrated on the synthesis and characterization of the following superhard materials:

1. Carbides

a) Carbides of tungsten since they have the highest hot hardness of all carbides.

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b) HfC since it has the second highest hot hardness and has been reported to be a good cutting tool coating for machining titanium.

c) Boron carbide since it is a very hard material in current usage.

d) Mixed carbides in the system VC-TiC. Jangg et al[4] report a maximum in hardness at TiC - 30% VC.

e) Mixed carbides in the system TaC-HfC. The TaC-20% HfC alloy has the highest reported melting point of all alloys.

f) Mixed carbides in the system TiC-ZrC. "Alloys" in this system are reported to be harder than TiC. It is also an experimentally easy alloy to evaporate and will serve as a model system for studying mixed carbides.

2. Nitrides

The synthesis of cubic boron nitride will be attempted since past work has shown that it is possible to synthesize β-SiC[5] which is also cubic. Success would provide an alternate and possible cheaper method of producing a proven hard material.

3. Oxides

a) Al_2O_3 since this is a commercially used grinding material, and will be used as a model system.

b) Mixed oxides in the system Al_2O_3-ZrO_2 to produce fine grained two-phase structures of different morphology[6] harder than the pure oxides.

4. Two-Phase Alloys

a) TiC + B and VC + B - a tenfold increase in strength has been reported due to precipitation hardening.

b) Ultrafine grained cermets-carbides in a matrix of metal or alloy in an effort to improve the toughness of the carbides. The present-day cermets have a lower limit of 3 μ in carbide particle size. The toughness

increases very rapidly as the size of the carbide becomes smaller. Such a very fine grained cermet coating would be expected to retain the cutting ability of the hard carbide while improving its resistance to fracture. Preliminary work at UCLA has shown the ability to synthesize TiC-Ni cermet coating using the ARE process. As a further step, resistance to degradation at high tool tip temperatures would be improved by substituting a more refractory metal for the ductile matrix in the cermet.

c) High temperature ultrafine grained cermets-carbides in a matrix of refractory metal to improve the hot hardness of the composite structure.

The important process variables that will be studied are:

1. Substrate temperature which affects grain size, density, particle size in two-phase alloys and residual stresses. The range of substrate temperatures to be explored is 500-1500°C.

2. Heat treatment - to study annealing effects in single phase material and to study precipitation effects where applicable.

Substrate materials will be a metal and/or ceramic. Deposit thickness will be about .001-.005" so as to assure bulk properties.

Characterization of the synthesized materials will be carried out by the following:

1. Microhardness at room and elevated temperature.

2. Chemical analysis using the microprobe, the non-dispersive detector and other analytical techniques as required.

3. Microstructure using optical, scanning and transmission electron microscopy.

4. X-ray diffraction to measure precision lattice parameters, "particle size" and residual stresses. Computer programs have been developed at UCLA to handle the X-ray data.

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5. Density.

At the start of the project, a preliminary study will be run to explore the synthesis of the various materials followed by limited characterization (lattice parameter, microhardness and structure as a function of C/M ratio) to aid material selection for detailed studies.

B. <u>Effect of Superhard Coatings on Cutting Tool Performance</u>

During metal cutting, tool damage can be due to tool wear (flank and crater wear), and/or cracking along the tool face. The tool must support the cutting forces at the high temperatures attained during cutting, and it must also endure the cyclic thermal stresses induced by the cutting, non-cutting cycle. Such conditions call for a tool material that is both hard and tough and resistant to wear.

During this phase of the research program, high speed steel tools will be coated initially with TiC and subsequently with other superhard materials developed in the first part of this program. The coating will provide the necessary hardness and wear resistance while the core, which is the high speed steel tool in this case, will provide the toughness and the resistance to impact loading. Machining tests will be carried out on the coated tools at different conditions of cutting speeds, feed, and depth of cut. Intermittant as well as non-intermittant tests will be employed. The cutting forces will be measured in each case using a tool dynamometer. The tool work interface temperature and friction coefficient along the tool face will be determined. Tool damage and surface finish of the machined part will be examined. Tool life will be determined. The wear process and mechanism of the different coatings will be investigated using tool-maker's microscope, scanning electron microscope techniques, and electron microprobe analyses. The crater and flank wear heights will be measured at different locations. The scanning electron

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microscope brings out topographical details of tool wear, cracks, and failure with more clarity and detail than one can observe with an optical microscope. While a SEM photograph provides fine details of tool surfaces, it is still necessary to have the electron microprobe analysis for identification of specific elements in the worn tool surfaces which then helps to understand the contact interactions between workpiece and tool. Correlation between microstructure and mechanical properties of the coating and the core material to their cutting performance will also be examined. Comparison of the cutting forces, temperature, friction coefficient, surface finish of the machined part, and tool wear will be examined and correlation to the physical and mechanical properties of the different coatings will be carried out.

Tool damage vs. cutting speed for a given feed and depth of cut will be compared for different tool coatings. Wear measurements will be obtained from direct comparison of the tool contours before and after test. Correlation of tool wear results to parameters characterizing the coating (coating composition, grain size, density, lattice parameter, coating thickness, microhardness and C/M ratio) will be investigated. Such correlation will constitute the feedback information for the synthesis of the superhard coating materials.

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III.   PROGRESS TO DATE

During the period October to December 1975, the rate of progress on the research work was much slower since the funds had practically ran out, and we were operating under a no-cost extension from July 1 to December 31, 1975. An extension of the contract was approved with a starting date of January 1, 1976. The majority of the work reported therefore is for a three month period, January 1 to March 31, 1976.

Work during this period was concentrated in the following areas:

1.   Synthesis of Fine-Grained TiC-Ni Cermets

This work was described in a prior report UCLA-ENG-7559. At that time, we were unable to resolve the microstructure of the cermet deposit. This work was completed and a paper written and presented at the International Conference on Metallurgical Coatings, San Francisco, California, April 1976. It is included as Appendix I of this report. The principal conclusion is that cermets synthesized by the ARE process have a markedly different microstructure from those prepared by powder metallurgy techniques. In the latter case, e.g. WC-Co or TiC-Ni, the metallic component Co or Ni is primarily present as a matrix phase surrounding the carbide phase particles. In the TiC-Ni cermet deposited by ARE, the structure consists of fine grained TiC with very small particles of Ni-Ti solid solution or Ti_2Ni dispersed throughout the structure. This type of microstructure would be of potential interest in increasing the toughness of ceramics.

2.   Synthesis of Al_2O_3 Deposits by the ARE Process

Work on this aspect was completed and also presented as a paper at the International Conference on Metallurgical Coatings. A complete text is appended to this report as Appendix II. The principal conclusions of this report were

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that α-Al_2O_3 deposits can be successfully produced by the ARE process at higher deposition temperatures. At lower temperatures, the Al_2O_3 is amorphous or a mixture of amorphous and α-Al_2O_3.

3. Synthesis of VC-TiC Alloy Carbides

This work was continued and is still in progress. The results will be given in the next report.

4. Machining Evaluation of High Speed Steel

a) Measurement of Cutting Forces

A two component dynamometer to measure forces in two orthogonal directions was constructed, installed, calibrated and tested. Figure 1 shows a trace of the two components of the cutting force during a machining test.

b) Evaluation of Coated Cutting Tools

Cutting tests were run on 20 coated high speed steel (Type M43) inserts which had been purchased from a commercial producer. The scatter in the results was very large. The cause of this problem is most probably due to the poor quality of the cutting edge preparation in the commercially procurred insert. Figure 2 is a composite photomicrograph of an uncoated tool near a cutting corner. Figure 3 is a higher magnification shot of the corner. Note that the tool has been ground very poorly with numerous turned-up edges. As a result, the coating does not go to the very edge of the tool as it should (Fig. 4a) or breaks away very readily as shown in Fig. 4b. Attempts were made to regrind the inserts without success. Therefore, it was decided to purchase bars of high speed steel, heat treat them by hardening and tempering and prepare machining inserts at UCLA. In this way, we hope to have a reproducible substrate on which to deposit hard coatings and evaluate them. This work is underway. Unfortunately, there are no other suppliers of high speed tool steel inserts (1/2" x 1/2" x 3/8") in contrast to numerous suppliers for cemented carbide inserts.

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FEED = .003 ; DEPTH = .020 ; RPM = 200

(HORIZONTAL)

(VERTICAL)

TIME (SECONDS) →

75 lb

50 lb

100 lb

50 lb

HORIZONTAL 0 lb
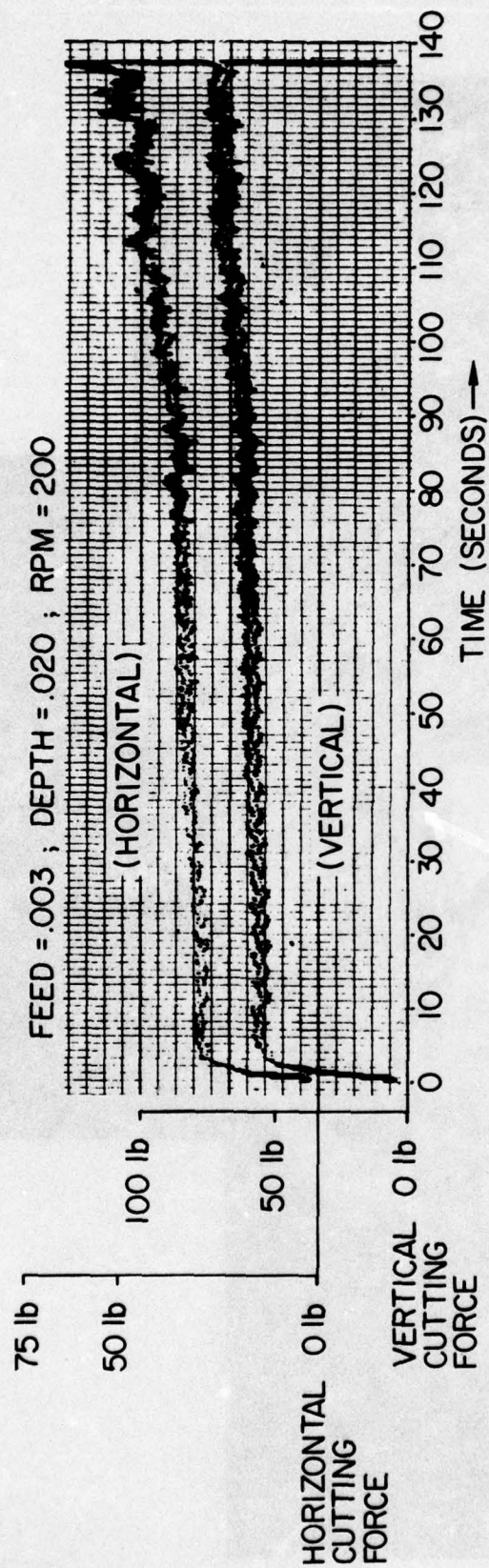CUTTING
FORCE

VERTICAL 0 lb
CUTTING
FORCE
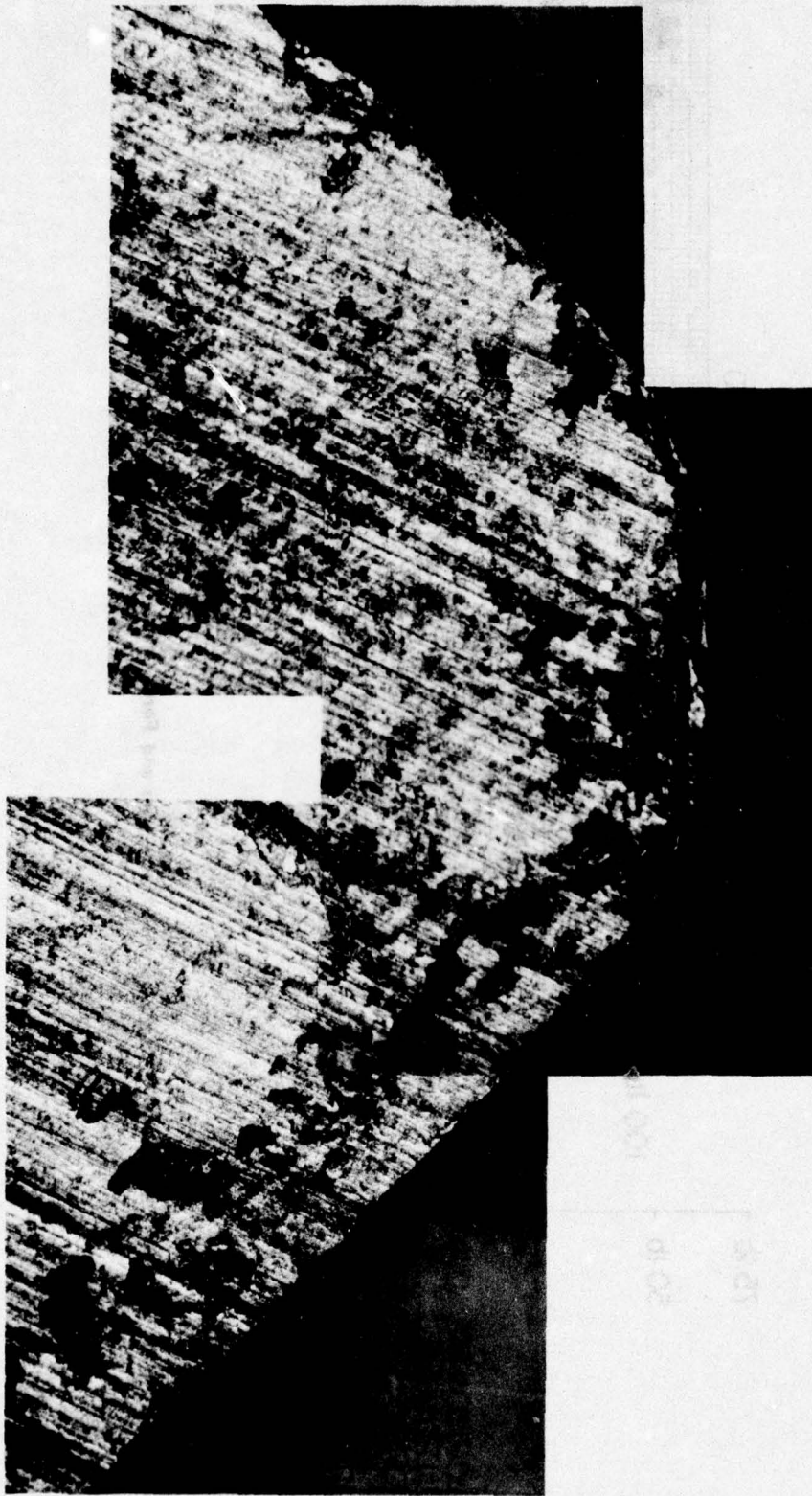
Figure 1. Tool Forces and Force Calibration Chart.

Figure 2. Uncoated M-43 High Speed Steel Insert Showing Rough Grinding, Poor Radius and Turned-up Edges (100X).
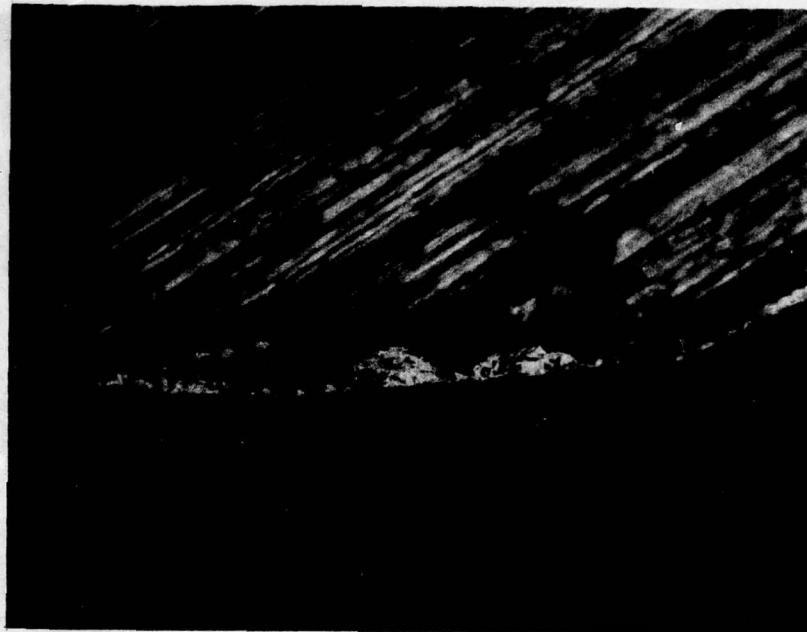
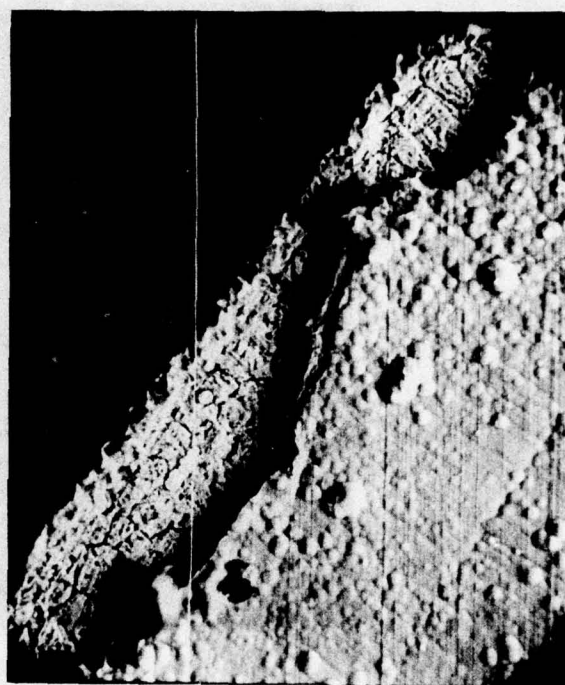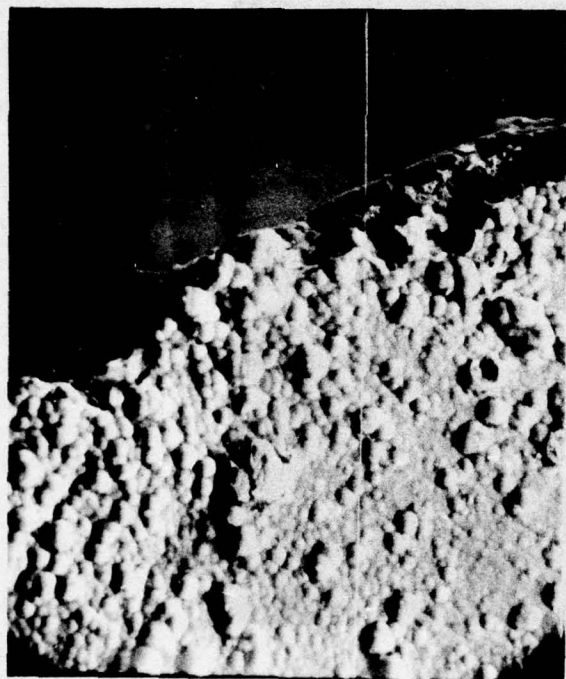Figure 3. Turned-up Edges on Uncoated Insert (500X).

Figure 4. Coated Insert with Coating Spalling at Edges Due to Turned-up
Edges on Uncoated Insert (500X).

IV. FUTURE RESEARCH EFFORTS

Research effort in the next period will consist of:

1. Synthesis and evaluation of TiC-VC, TaC-HfC, TiC-B.
2. Coating of high speed steel inserts with various coatings and then machining performance.

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APPENDIX 1

STRUCTURE OF TiC-Ni COATINGS SYNTHESIZED BY
ACTIVATED REACTIVE EVAPORATION

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ABSTRACT

TiC-Ni coatings were produced by evaporation of a Ti-Ni billet in the
presence of a partial pressure of C_2H_2 to produce a TiC-Ni deposit using
the Activated Reactive Evaporation process. The coatings were characterized
by x-ray diffraction, optical, scanning and transmission electron micro-
scopy as well as microhardness measurements. The microstructure consists
of a dispersion of very fine particles of Ti_2Ni and Ni-Ti solid solution
in a TiC matrix. The grain size of the TiC can be controlled by varying
the deposition temperature. This microstructure might be very desirable
for increasing the toughness of ceramic coatings.

INTRODUCTION

The need for improved materials in high temperature structural applications has stimulated considerable interest in refractory cemented carbide based composites. These materials are essentially aggregates of particles of refractory metallic carbides sintered together by an iron group metal. The properties of these composites are derived from those of their constituents, namely, the hard and brittle carbide and the soft, ductile binder. The most commonly used among this group of composites are TiC-Ni and WC-Co. Owing to the superior oxidation resistance and lower density of the TiC-Ni composites, these are more attractive for certain applications, such as turbine blades.

Liquid phase sintering is, at present, generally used for the fabrication of these composite materials. This, can have a significant difference on the material behavior since pores provide fracture sources and reduce strength. To try and avoid porosity and obtain a finer grain size for increased toughness, some preliminary experiments were done on the synthesis of TiC-Ni composites by the activated reactive evaporation (ARE) process. [1] This investigation further characterized the structure of these deposits.

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EXPERIMENTAL PROCEDURE

A Ti-10 Ni alloy rod was evaporated by electron beam heating in the ARE reactor as previously described by Bunshah and Raghuram.[2] C_2H_2 was introduced into the system after steady state conditions of evaporation had been attained.[3] The conditions of deposition are given in Table I. Ta sheet was used as a substrate in both cases.

Table I

Nominal Conditions of Synthesis

Sample No.	Emission Current (A)	Evaporation Rate (g/min)	C_2H_2 Pressure (torr)	Deposition Temperature (C°)	Microhardness KHN 50g load Kg/mm^2
1	0.20	0.32	$1.1-1.2 \times 10^{-3}$	1000	2810
2	0.20	0.21	$1.2-1.3 \times 10^{-3}$	700	2050

The specimens were characterized by optical microscopy, x-ray diffraction analysis, electron microprobe analysis, and transmission electron microscopy. Specimens were thinned by ion-milling for TEM examination.

RESULTS AND DISCUSSION

The deposits exhibited a typical columnar morphology with the grain diameter increasing with the deposition temperature. X-ray diffraction analysis showed the presence of TiC and Ni in the deposit but no intermetallic compounds like Ti_2Ni probably because the particle size is too small.

The 1000°C specimen showed a distribution of particles in the TiC matrix except in the region near the Ta substrate. Figure 1 shows the composition profile and X-ray images for Ti, Ta and Ni across the thickness

Figure I. - Microprobe analysis of a "ARE"
Ti-10% Ni-C coating, deposited at a 1000°C

Quantitative microprobe analysis (in wt %) using
"Magic" correction.

Element	1	2	3	4
Ti	1.82	12.33	81.00	73.84
Ni	35.39	5.53	1.73	9.35
C	?	8.04	17.27	16.81
Ta	55.70	74.75	–	–
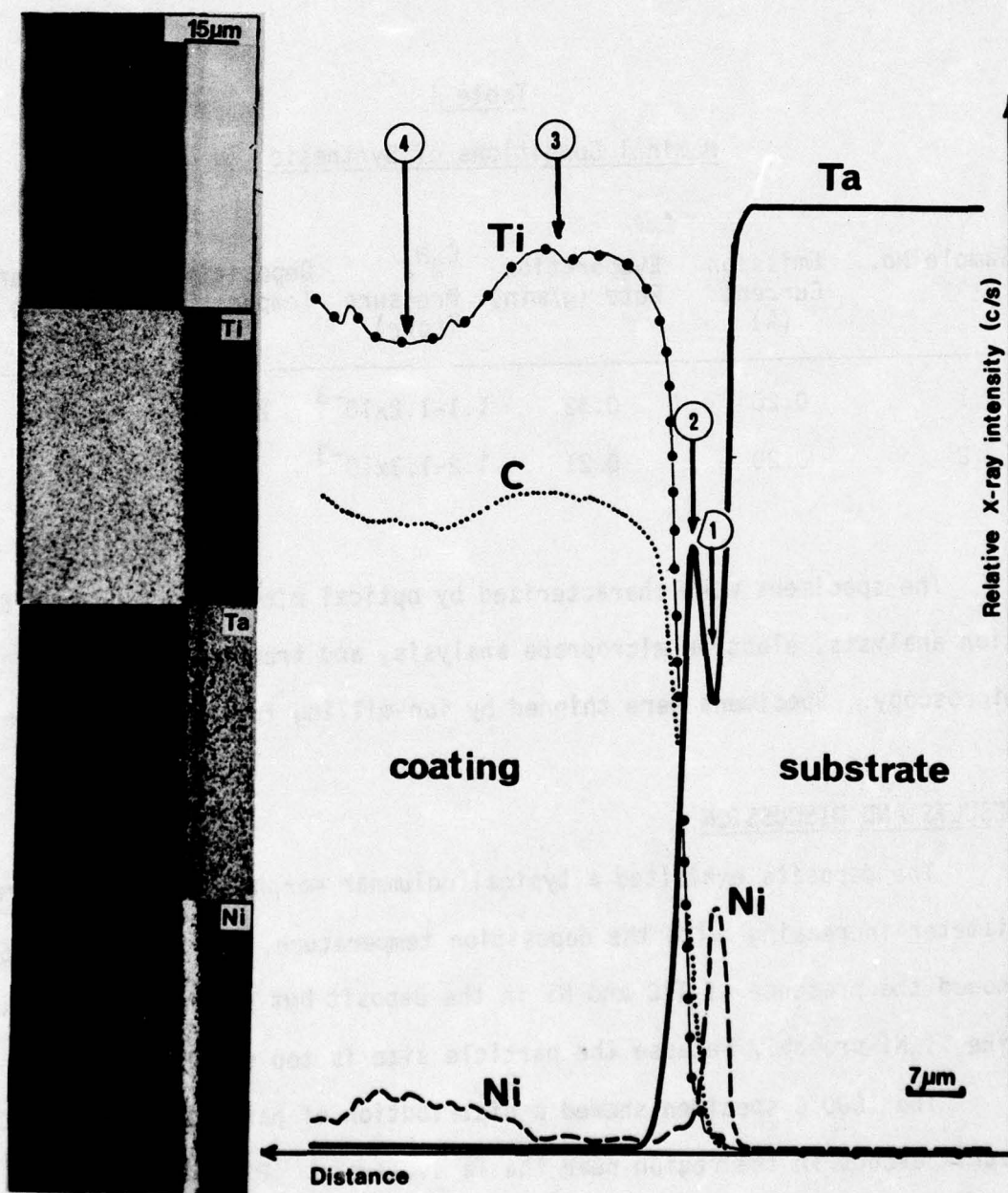
of the deposit. It may be noticed that there is a depletion of Ni in the deposit next to the substrate deposit interface and a concentration of Ni in the Ta substrate next to the interface. This can be attributed to the diffusion of Ni along the columnar TiC grain boundaries into the substrate (in this case Ta). The composition at point 1 (Figure 3) is very close to the intermetallic compound $\gamma(Ni_2Ta)$.

Figures 2 and 3 show the structure of the 1000°C coating in transmission. The location of the foil is between points 3 and 4 (Fig. 3) Apart from a few coarse particles at the TiC grain boundaries (Fig. 5) the particles were generally found to be concentrated in the core of the TiC grains. As mentioned earlier, this depletion around the TiC grain boundaries is caused by grain boundary diffusion of Ni towards the Ta substrate during growth. Owing to volume diffusion (which is probably much slower) within the TiC grains some particle coarsening is also visible.

Extensive analysis on the particles were performed in the TEM. Using a STEM system with an EDS analyzer, quantitative analysis of the compositon of the particles (for Ni and Ti) was obtained. Unlike previous observations [1] these results showed that the particles had a wide range of composition variation (anywheres between 60 and 80 weight percent Ni). The composition close to the intermetallic Ti_2Ni was found to be the most predominant. Guinter X-ray analysis on the thin foils confirmed the presence of Ti_2Ni (with a lattice parameter of $11.320 \pm 0.005°A$). The lattice parameter of TiC in the 1000°C deposit was found to be $4.332 \pm 0.005°A$.

Figures 4 shows the concentration profiles for Ti, C and Ni for the 700°C deposit. Figures 5 and 6 are TEM photomicrographs showing the structure of this deposit. As is evident, the grain size of this deposit is several orders of magnitude finer than the 1000°C (Figures 2 and 3) deposit. The de-

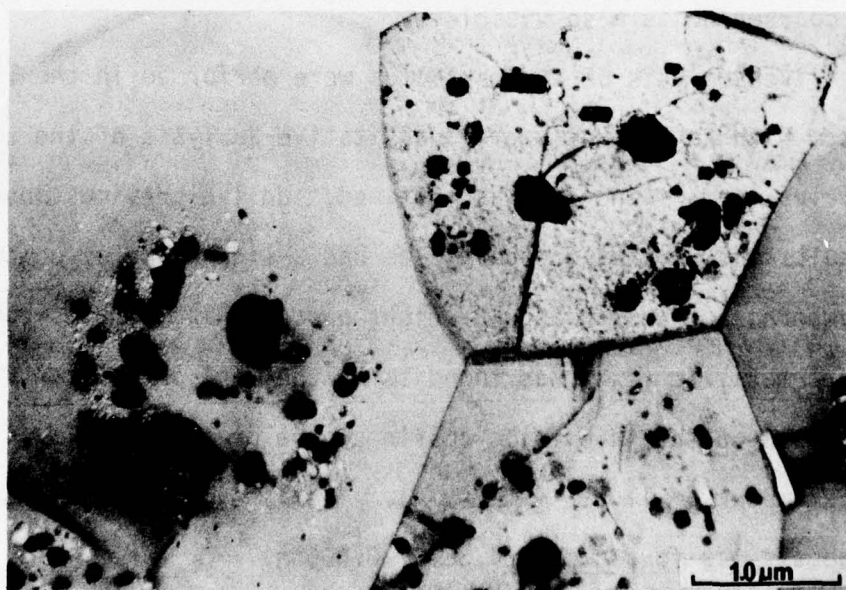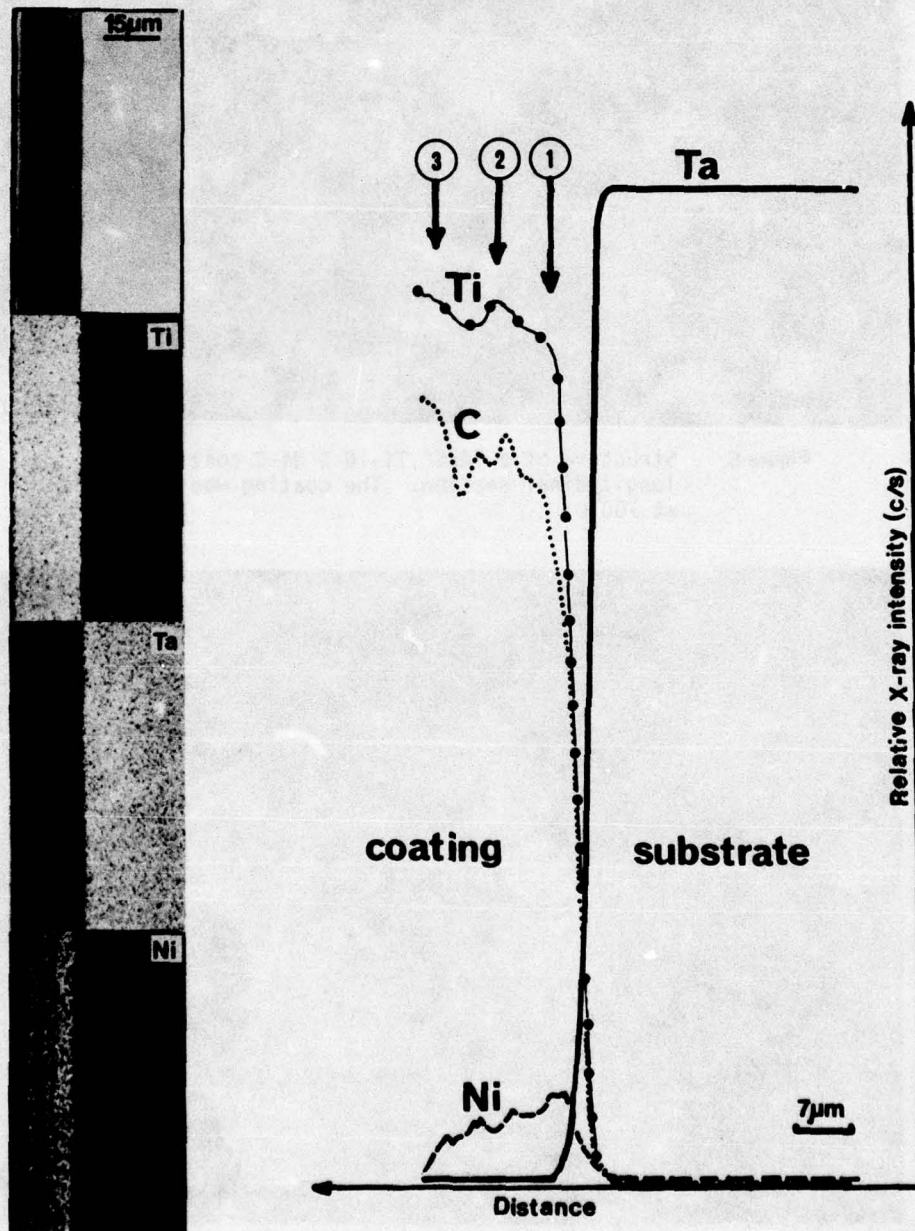Figure 2 - Structure of a "ARE" Ti-10 % Ni-C coating in a longitudinal section. The coating was deposited at a 1000°C.

Figure 3 - The pressure of dislocations inside TiC grains around Ti$_x$Ni$_y$ particles. (Ti-10 % Ni-C coating deposited at a 1000°C).

Figure 4 - Microprobe analysis of a "ARE"
Ti-10% Ni-C coating, deposited at 700°C

Quantitative microprobe analysis (in wt %) using
"Magic" correction.

Element	1	2	3
Ti	71.55	75.97	78.21
Ni	11.18	7.49	1.89
C	17.27	16.54	19.90

Figure 4 - Microprobe analysis of a "ARE"
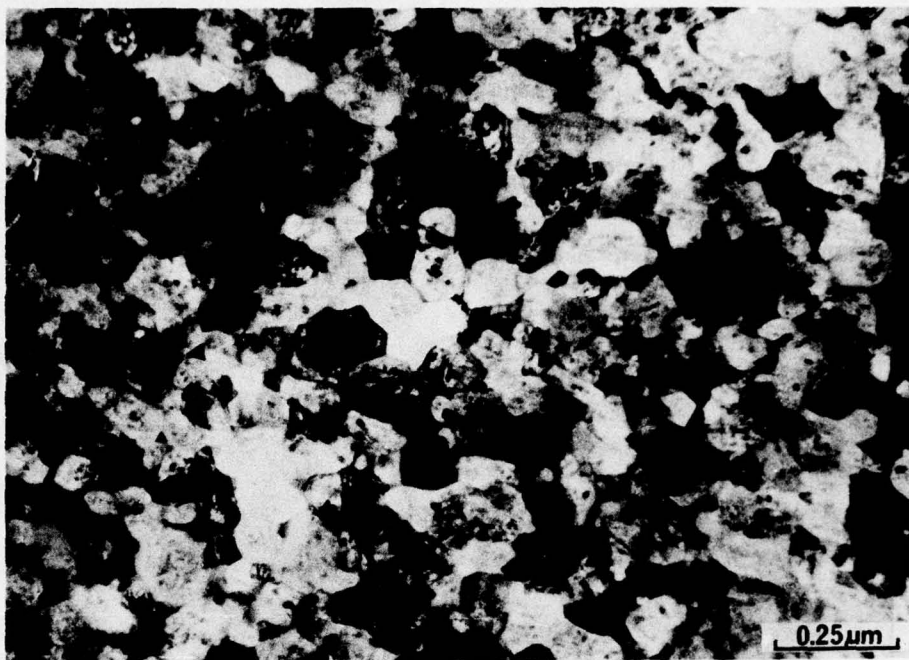Ti-10% Ni-C coating, deposited at 700°C

Figure 5. - Structure of a "ARE" Ti-10 % Ni-C coating in a longitudinal section. The coating was deposited at $700°$ C.
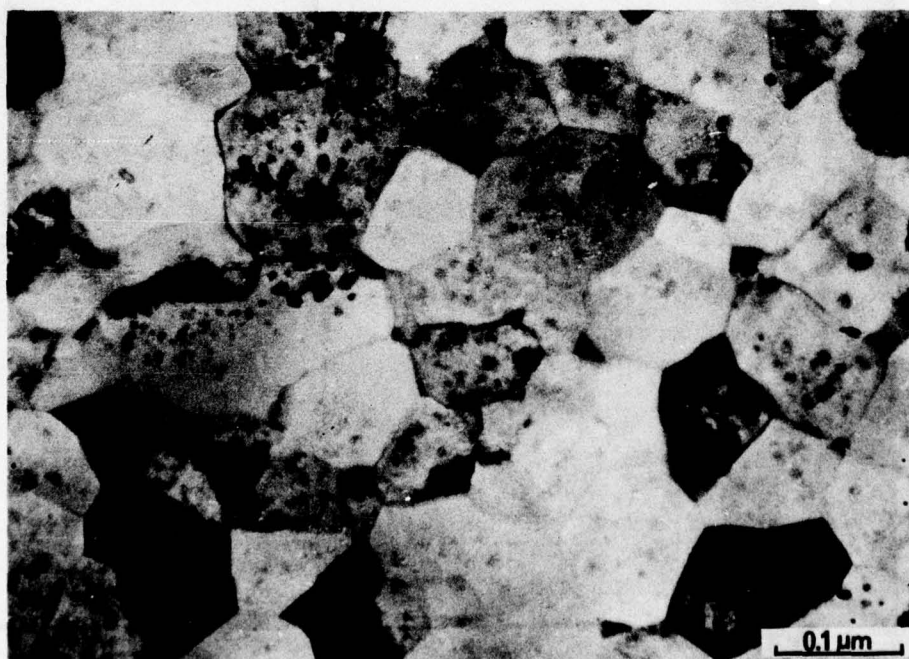

Figure 6. - Dispersion of fine $Ti_x Ni_y$ particles in a "ARE" Ti-10 % Ni-C coating, deposited at $700°$C.

posit was found to have a very fine and relatively homogeneous distribution of Ti-Ni intermetallic and Ni-Ti solid solution particles (Figures 6). Unlike the 1000°C deposit, segregation effects owing to diffusion of Ni were not visible in the 700°C sample. Owing to their size an accurate STEM analysis of their composition could not be done, but Guinier X-ray analysis on the thin foil showed the presence of Ti_2Ni with a lattice parameter of 11.340 ± 0.005°A. The lattice parameter of the TiC was found to be 4.335 ± 0.005°A.

The lattice parameter of the TiC in both the deposits was found to be higher than stoichiometric TiC (a = 4.325°A). The maximum lattice parameter reported is 4.3305 ($TiC_{0.86}$)[4]. This does not indicate that the deposits contain non-stoichiometric TiC, since lattice parameter increases can also be due to some Ni in solid-solution in the TiC. EDS analysis on the 1000°C deposit in the stem did indicate the presence of Ni in particle free areas of TiC (Figure 6).

CONCLUSION

The present results indicate that unlike sintered cemented TiC-Ni composites, synthesis by ARE results in fine particles of Ti-Ni intermetallics and of Ni-Ti solid solution dispersed throughout the TiC grains. The TiC matrix also contains Ni in solid solution. The grain size of TiC is easily controlled by the deposition temperature. Ni diffuses into the substrate during the coating process, which leads to an extremely adherent diffusion bond. Further work on synthesis of such composites could lead to fine grained, tough, oxidation resistant material for tool coatings and high temperature uses.

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APPENDIX 2

ALUMINA DEPOSITION BY ACTIVATED REACTIVE EVAPORATION

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Abstract

Alumina deposits were synthesized at various deposition temperatures from 700 to 1200°C using the Activated Reactive Evaporation process by evaporating aluminum in the presence of a partial pressure of oxygen. The deposits were characterized by x-ray diffraction, scanning electron microscopy and microhardness measurements. The structure is predominantly amorphous at lower deposition temperatures and the equilibrium α-Al_2O_3 at higher deposition temperatures. The results compare closely to Al_2O_3 deposits produced by Direct Evaporation and Sputtering.

Objective

The objective of this investigation was to investigate the experimental parameters for the deposition of alumina thick films by the Activated Reactive Evaporation (ARE) process,[1,2] and their influence on the structure and morphology of the deposits

Background Information

Thin or thick film deposits of refractory compounds can be produced by Direct Evaporation[3,4,5] Reactive Evaporation,[6,7,8,9,10] Direct Sputtering from a refractory compound target, [11] Reactive Sputtering[12,13] and Chemical Vapor Deposition.[14] In certain cases, they can also be produced by thermal or electrolytic treatments of metal surfaces, e.g., anodization of aluminum to produce alumina.[13] In direct Evaporation and Sputtering, the evaporant or target is the same material as the deposit, e.g., Al_2O_3 to deposit Al_2O_3. In Reactive Evaporation or Sputtering, the evaporant or target is a metal or lower oxide which reacts with O_2 provided by a gas bleed into the vacuum chamber to form the oxide; e.g., Al is evaporated in the presence of O_2 gas to form Al_2O_3 or SiO is evaporated in the presence of oxygen to form SiO_2.

At least seven forms of alumina have been reported but six of these forms have been traditionally designated "gamma" alumina.[15] Transformation to a more stable high temperature form, alpha alumina, occurs in the range 750 to 1200°C. Alpha alumina crystallizes in the hexagonal system and has a melting point of 2050 ± 20°C, whereas gamma alumina crystallizes in the cubic system.

All the above-mentioned techniques have been used to produce thin films of alumina at low deposition rates with the exception of the work of Movchan and Demchishin[4] who deposited alumina at high rates by Direct Evaporation of a sintered compact of alumina using a high power density electron beam. In

Reactive Evaporation, the oxidation of Al to Al_2O_3 is not always complete as was reported by DaSilva and White,[6] the film properties changing further after exposure to the atmosphere. H_2O vapors can also be used instead of oxygen in Reactive Evaporation.[9,10] The Al_2O_3 films were clear and approaching stoichiometry when sufficient water vapor was present, became brown and opaque when the ratio of water vapor to aluminum fell below 1.5 and metallic when this ratio was less than unity.[9] Similarly for Direct Evaporation, Hoffman and Leibowitz[5] found that their films were dark and deficient in oxygen which could be remedied by introducing a small partial pressure of oxygen approximately 10^{-4} torr into the vacuum chamber during evaporation.

The Activated Reactive Evaporation process[1,2,16] is a way of depositing films of refractory compounds at high rates by evaporating metals in the presence of the appropriate reactive gas to form the compound. The vaporized metal atoms and gas molecules are activated and/or partially ionized by a low pressure plasma generated in the space between the source and substrate with the help of a positively biased probe.[1] An advantage of this process is that the stoichiometry of the compound deposit can be easily varied and controlled as was demonstrated for TiC, ZrC and HfC deposits.[17] Colen and Bunshah[18] recently described the synthesis and properties of Y_2O_3 produced by evaporation of Y in the presence of O_2 using the ARE process.

Experimental Conditions

Figure 1 shows a schematic of the ARE process. A one inch diameter billet of 1100 S grade aluminum was evaporated from a rod fed electron beam source in the presence of a partial pressure of 99.5% pure oxygen gas which was varied from 2×10^{-5} torr to 2×10^{-4} torr. The substrates were stainless steel, tantalum and alumina at 700°C and 800°C deposition temperature which were obtained by using radiant heating. For higher depositon temperature of 1100°C
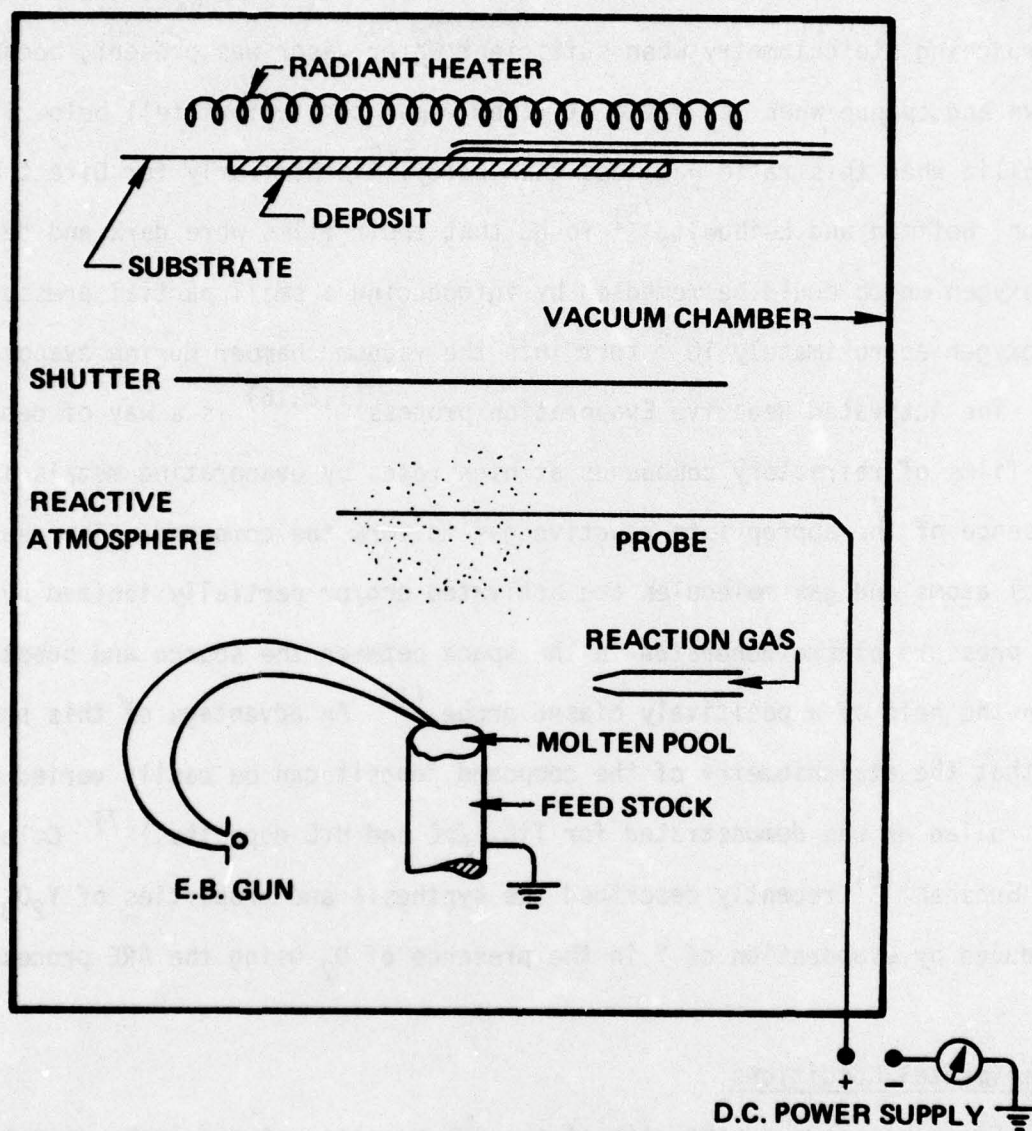
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Figure 1. Schematic of the Experimental Arrangement for the Activated Reactive Evaporation Process.
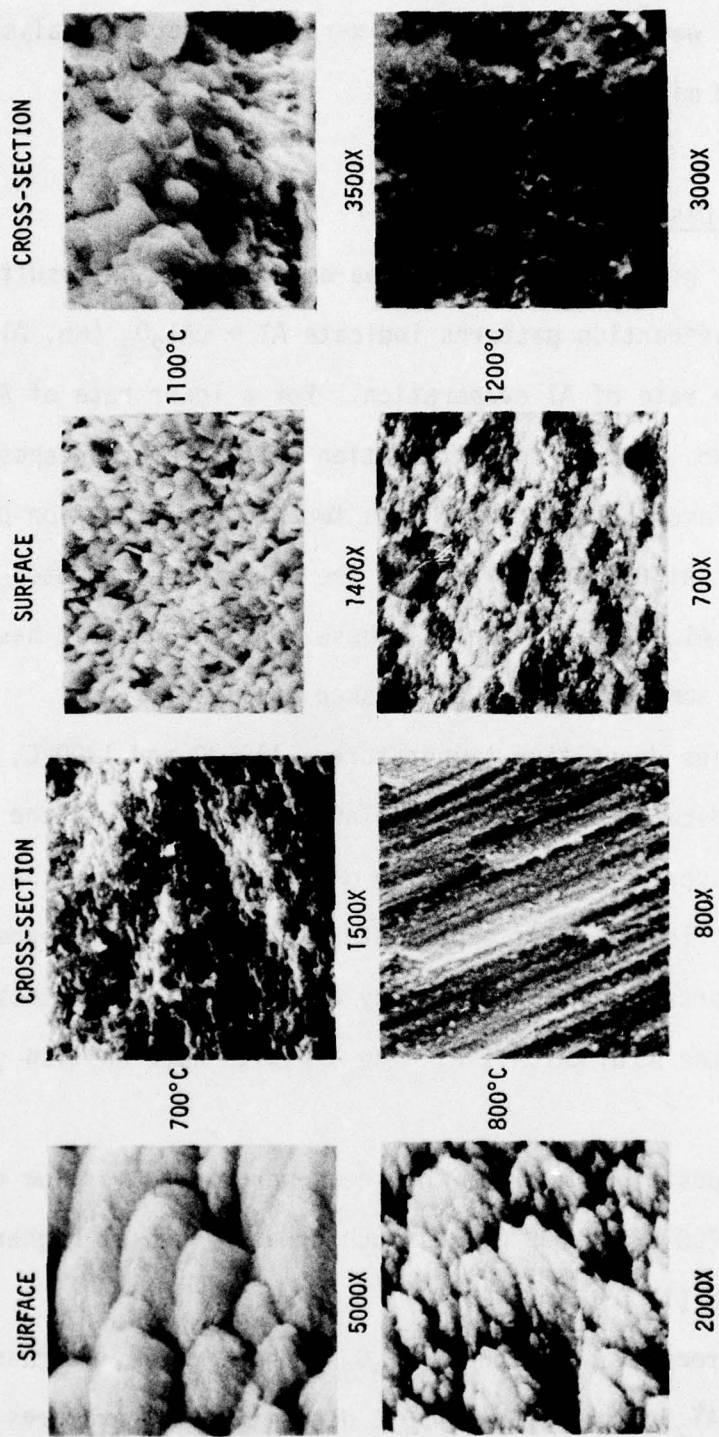
Figure 2: Structure of Alumina deposits at various deposition temperatures.

and 1200°C, a Ta foil substrate was used and heated by direct resistance. The deposits were characterized by x-ray diffraction analysis, microstructural analysis and microhardness.

Results and Discussions

Table I gives the deposition parameters and the results. At 700°C the x-ray diffraction patterns indicate Al + γAl_2O_3 (No. Al-D-2) indicating an excessive rate of Al evaporation. For a lower rate of Al evaporation at 700°C, Run No. Al-D-3, the diffraction pattern of the deposit was characteristic of an amorphous material with two broad diffraction peaks corresponding to γ-Al_2O_3. At 800°C, Run Al-D-4, the structure indicated was amorphous plus some γ-Al_2O_3 peaks. In all these runs the deposit has a milky white appearance, somewhat porous and flaked easily.

At higher deposition temperatures, 1100°C and 1200°C, the diffraction patterns indicated α-Al_2O_3 and Al TaO_4. The latter is the result of a diffusion layer formed between the α-Al_2O_3 deposit and the Ta substrate as is shown in Fig. 2. Lattice parameters of the α-Al_2O_3 deposits were measured and are reported in Table II. They are quite close to those reported for α-Al_2O_3 in the ASTM card file. The deposits were whitish grey, dense and adherent.

The deposition rate (μm thickness per minute) at low deposition temperatures (700°C and 800°C) was much greater than at higher deposition temperatures (1100°C and 1200°C).

For Direct Evaporation of Al_2O_3 at high rates, Movchan and coworkers[19] reported γ-Al_2O_3 from 300 to 450°C deposition temperatures appearing as a clear film, a coarse flaky crystalline deposit of α-Al_2O_3 from 450 to 900°C and a dark adherent α-Al_2O_3 deposit above 900°C. Similarly, Thornton and Chin[20] reported that sputtered Al_2O_3 deposits were amorphous below 665°C

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deposition temperature, appeared in the metastable gamma form between 665°C and 1251°C and in the equilibrium alpha form above 1251°C.

The results on the crystalline form of Al_2O_3 deposits as a function of deposition temperature for the three different physical vapor deposition techniques appear to be very similar.

Fig. 2 shows the surface and fracture cross-section of the deposits at various deposition temperatures. At the lower deposition temperatures 700°C and 800°C, the surface appears as clusters of pyramidal crystals and the cross-section shows a very fine acicular structure. At higher deposition temperatures, the surface appearance is modular and cross-section somewhat coarser grained. It is hard to draw a correlation with the Movchan-Demchishin zones[4] reported by those authors in an earlier paper for Al_2O_3 deposits produced by Direct Evaporation, nor is it possible to make direct comparison since no structures were shown in the Movchan and Demchishin paper.[4]

The microhardness of the 1100°C and 1200°C deposition temperature specimens ranged from 500 to 800 kg/mm^2 VHN. These are very similar to the values reported by Movchan and Demchishin for the Al_2O_3 deposits produced by Direct Evaporation at the same temperatures.

Conclusion

Alumina coatings have been produced by the Activated Reactive Evaporation process. The crystal structure and microstructure vary with deposition temperatures. At the lower deposition temperatures, 700 and 800°C, the deposit is amorphous with some indications of the presence of gamma alumina. The equilibrium $\alpha-Al_2O_3$ structure is deposited at higher deposition temperatures 1100°C and 1200°C. The results on structure and microhardness are comparable to those produced by Direct Evaporation and Sputtering.

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TABLE I: Deposition Parameters for Al_2O_3

Run No.	Deposition Temperature (°C)	Phases Present by X-Ray Diffraction	Deposit Thickness (μm)	Condensation Time (min)	O_2 Gas Pressure (torr)
Al-D-2	700	60% Al-40% γ-Al_2O_3	100	11	3×10^{-4}
Al-D-3	700	Amorphous Pattern +2 broad γ-Al_2O_3 peaks	>300	20	3×10^{-4}
Al-D-4	800	Amorphous Pattern +2 very small γ-Al_2O_3	200	8	7×10^{-5}
Al-D-5	1200	α-Al_2O_3+$AlTaO_4$	25	10	2×10^{-4}
Al-D-6	1100	α-Al_2O_3+$AlTaO_4$	25	15	2×10^{-4}
Al-D-7	1100	α-Al_2O_3+$AlTaO_4$	25	15	2×10^{-5}
Al-D-8	1100	α-Al_2O_3 (trace) +$AlTaO_4$ (no plasma-R.E. process used)	25	15	2×10^{-5}

TABLE II: Lattice Parameter of α-Al$_2$O$_3$ Deposits

Run Number	Deposition Temperature (°C)	a(A°)	c(A°)	c/a
A1-D-5	1200	4.750	13.001	2.74
A1-D-6	1100	4.750	12.89	2.71
A1-D-7	1100	4.748	12.97	2.73
ASTM Card File		4.758	12.991	2.730

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